

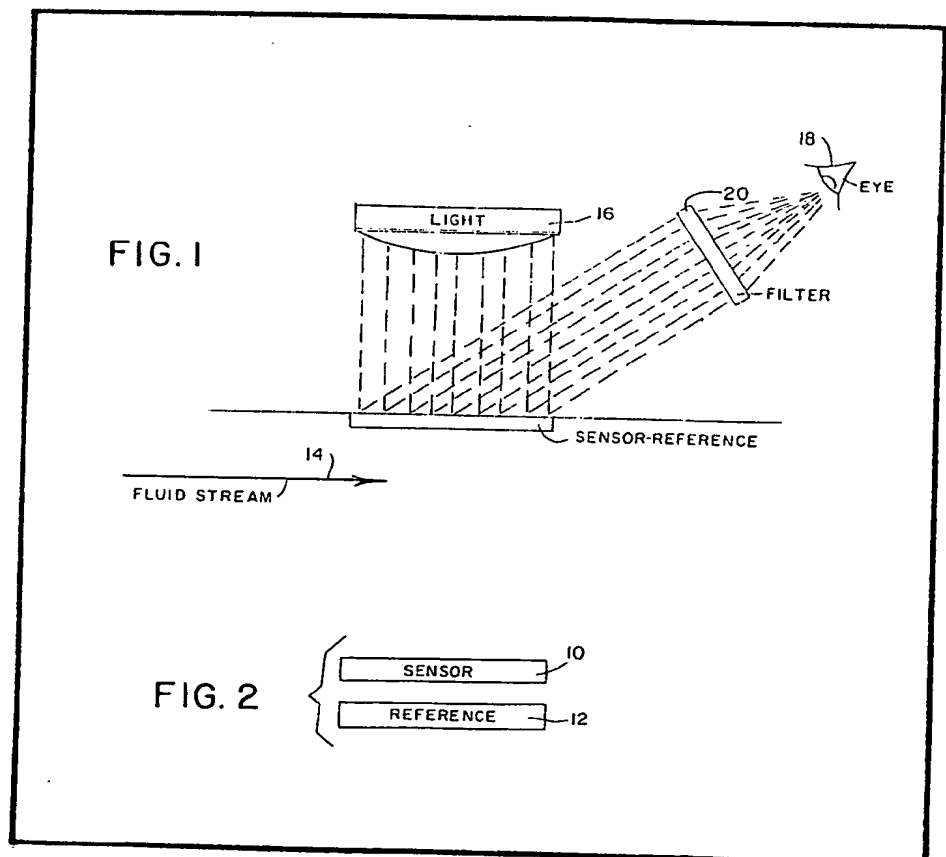
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(54) Method and apparatus for determining the presence of oxygen

(57) An oxygen sensor (10) has an inorganic complex, usually a complex of platinum group metals, with α -diimine ligands immobilized in a polymer support. The metal complex is a luminescent material quenchable by oxygen. The polymer is permeable to oxygen and impermeable to interfering quenchers. Oxygen concentration in a gaseous or liquid environment is determined by exposing the sensor to the environment and measuring the

quenching-related decrease in intensity or lifetime of luminescence. In one version, a reference device (12) has areas of differing depth or concentration of luminescent material immobilized in a support which is relatively impermeable to oxygen. Matching the luminescence of the sensor (10) with the luminescence of an area of the reference device (12) determines the extent of quenching and the concentration of oxygen. An alternative sensor has a mixture of luminescent materials having differing sensitivities to oxygen quenching and differing colours of emission.



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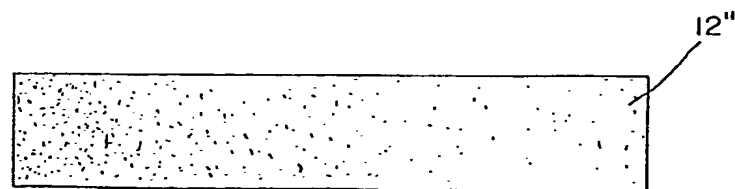
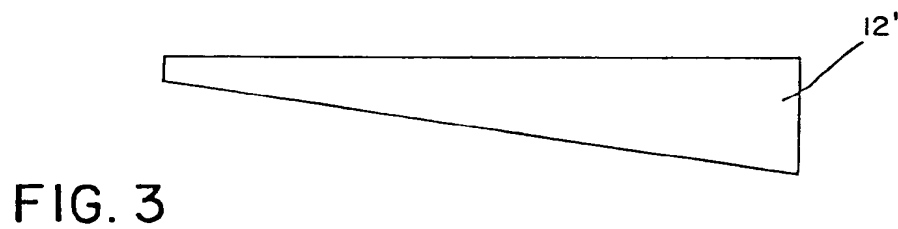
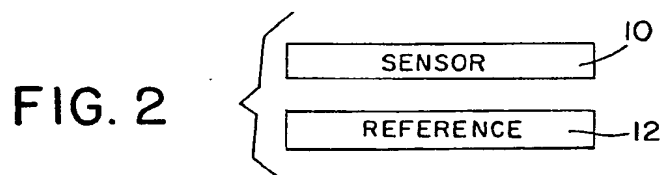
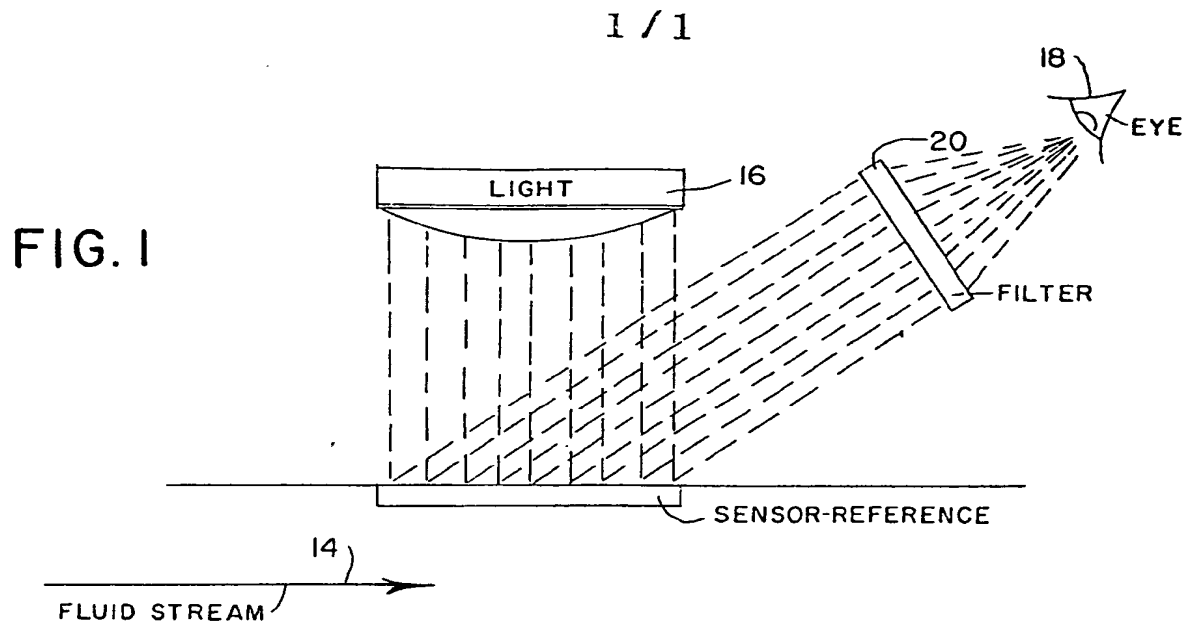


FIG. 4

SPECIFICATION

Method and apparatus for determining the presence of oxygen

5 This invention relates generally to a method and apparatus for determining the presence and concentration of oxygen in a gaseous or liquid environment and is based on the principle of luminescence quenching.

10 The two most common methods currently used for determining oxygen concentrations are the Winkler titration method and the oxygen electrode method. The Winkler method is slow, intrusive, destroys the sample and does not lend itself to automation. The oxygen electrode method consumes oxygen, is sensitive to interferants such as Halothane anaesthetic, is intrusive, and is not readily applicable to the gas phase or vacuum systems. Hence, neither of these methods is particularly desirable.

20 It is known that many platinum group metal complexes luminesce intensely in the red region (600—650 nm) when excited with visible light or UV light (<550 nm). Both the intensity and the lifetime of the luminescence is decreased when the complex is exposed to deactivators (quenchers). Oxygen, iron (III), copper (II), and mercury (II) are among the common quenchers. When a single quencher is present in an environment, the degree of intensity or lifetime quenching is directly related to the quencher concentration and can be used as an analytical method for determining that concentration. However, the inability of the method to discriminate among different quenchers in an environment has heretofore prevented the method from being universally applicable.

35 The discrimination problem is particularly acute when dealing with a liquid environment. If the luminescent complexes are dissolved directly in the solution, a variety of dissolved organic and inorganic, contaminants and interferents would contribute to the quenching and would produce an erroneous indication of the oxygen concentration.

45 Because the luminescence quenching method presents the possibility of making oxygen determinations without the limitations inherent in the Winkler titration method and the oxygen electrode method, it is desirable to improve upon known methods and apparatus in the luminescence quenching art in order to make that method universally applicable.

50 Examples of pertinent patents are U.S. Patent Nos 998,091; 1,456,964; 2,351,644; 2,929,687; 3,112,999; 3,697,226; 3,725,658; 3,764,269; 3,768,976; 3,881,869; 3,897,214; 3,976,451; 4,054,490; 4,073,623; 4,089,797; 4,181,501; 4,231,754; 4,260,392; 4,272,249; 4,272,484 and 4,272,485.

60 U.S. Patent 3,725,658 shows a method and apparatus for detecting oxygen in a gas stream. The apparatus employs a sensor film comprising a fluorescent material dissolved in a carrier or solvent and supported on a substrate. Oxygen

65 contained in the gas stream is dissolved into the film and quenches the fluorescent emission, the extent of quenching being proportional to the oxygen content of the gas stream.

70 U.S. Patent 3,764,269 shows the use of a gas permeable membrane which permits diffusion of a particular gas while providing protection against the adverse effects of the environment. An electrochemical device detects the concentration of gas which passes through the porous layer and activates the electrode.

75 U.S. Patent 3,881,869 discloses the chemiluminescent detection of ozone concentration in a gas sample. The gas sample contacts an organic polymer having a backbone chain consisting of carbon atoms to produce a chemiluminescent reaction. The concentration of ozone is proportional to the intensity of light emitted by the reaction.

80 U.S. Patent 4,089,797 discloses chemiluminescent warning capsules having an air-reactive chemiluminescent formulation encapsulated with a catalyst. Crushing the capsule mixes the air-reactive formulation and the catalyst in the external environment to produce chemiluminescence if air is present.

85 U.S. Patent 4,272,484 uses fluorescence methods to measure oxygen content after first separating blood protein fractions and other components by use of a gas permeable membrane. U.S. Patent 4,272,485 is a related disclosure which includes a carrier which transports particles through the membrane.

90 U.S. Patent 3,112,999 discloses a gas, particularly carbon monoxide, which permeates a porous layer to make an indication.

100 U.S. Patent 2,929,687 discloses a dissolved oxygen test.

U.S. Patent 3,768,976 shows a polymeric film through which oxygen migrates to cause an indication.

105 U.S. Patent 3,976,451 describes selectively permeable membranes for passing oxygen.

U.S. Patent 4,260,392 shows a selectively permeable plastic tape.

110 U.S. Patent 3,897,214 discloses reagents impregnated in plastic fibres.

U.S. Patent 3,697,266 discloses a system using a graded scale for visual comparison. The comparison scale is not placed in a solution. It is merely a screen.

115 U.S. Patent 998,091 discloses a colour comparing scheme in which thickness is varied in a graded standard.

U.S. Patents 4,181,501 and 4,054,490 disclose wedge shaped concentration sensors.

120 U.S. Patent 2,351,644 discloses a stepped sensor.

U.S. Patent 4,073,623 discloses a non-immersed sensor and standard used for visual comparisons.

125 U.S. Patent 1,456,964 discloses light intensity comparison.

The remaining patents are of lesser interest.

The following publications are also of interest:

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Energy Transfer in Chemiluminescence, Roswell, Paul and White, Journal of the American Chemical Society, 92:16, August 12, 1970, pp. 4855—60; *Oxygen Quenching of Charge-*

- 5 *Transfer Excited States of Ruthenium (II) Complexes. Evidence for Singlet Oxygen Production*, Demas, Diemente and Harris, Journal of the American Chemical Society, 95:20, October 3, 1973, pp. 6864—65; *Energy Transfer from Luminescent Transition Metal Complexes to Oxygen*, Demas, Harris and McBride, Journal of the American Chemical Society, 99:11, May 25, 1977, pp. 3547—3551; *Britton, Hydrogen Ions. Their Determination and Importance in Pure and*
- 15 *Industrial Chemistry*, D Van Nostrand Company, Inc. (1943) pp. 338—43; and *Fiberoptics Simplify Remote Analyses*, C & EN, September 27, 1982, pp. 28—30. *Porphyrins XVIII. Luminescence of (Co), (Ni), Pd, Pt Complexes*,
- 20 Eastwood and Gouterman, Journal of Molecular Spectroscopy, 35:3, September 1970, pp.359—375; *Porphyrins XIX. Triplet and Quartet Luminescence in Cu and VO complexes*,
- 25 Gouterman, Mothies Smith and Caughey, Journal of Chemical Physics, 52:7 April 1, 1970, pp 3795—3802; *Electron-Transfer Quenching of the Luminescent Excited State of Octachlorodirehenate (III)*, Nocera and Gray, Journal of the American Chemical Society 103, 1971, pp.
- 30 7349—7350; *Spectroscopic Properties and Redox Chemistry of the Phosphorescent State of $Pt_2(P_2O_5)_4H_8^{4-}$* ; Che, Butler, and Gray, Journal of the American Chemical Society 103, 1981, pp. 7796—7797; *Electronic Spectroscopy of*
- 35 *Diphosphine- and Diarsine-Bridged Rhodium (II) dimers*, Fordyce and Crosby, Journal of the American Chemical Society 104, 1982, pp. 985—988.

The Demas, *et al* articles disclose oxygen quenching of α -diimine complexes of Ru(II), Os(II), and Ir(III). 2,2'-Bipyridine, 1, 10-phenanthroline and substituted derivatives are used as ligands to form the metal-ligand complexes. A kinetic mechanism for the complex oxygen interaction is proposed.

The Roswell article discusses intermolecular energy transfer in chemiluminescence.

The Britton publication discloses a wedge method for the determination of indicator constants of two-colour indicators.

The C & EN article deals with PTFE control membranes in the context of laser optrodes and optical fibres.

The Eastwood article describes the room temperature luminescence and oxygen quenching of Pd and Pt porphyrin complexes in fluid solutions.

The Gouterman *et al*, article describes low temperature luminescence of Cu and VO porphyrins. Extrapolation of their data to room temperature indicates oxygen quenchable lifetimes.

The Nocera paper reports quenching of dinuclear Re species. Mononuclear and dinuclear

Re complexes also have quenchable excited states.

The Che paper reports long excited state lifetimes and solution oxygen quenching of a dimeric Pt complex in solution and long-lived quenchable excited states of Rh dimers.

The Fordyce reference reports long-lived low temperature emissions of Rh(II) with bridging ligands. Rh(II) and Ir(II) data are referenced. Extrapolation of their data to room temperature suggests oxygen quenchable lifetimes.

It is an object of the present invention to provide a method and apparatus which substantially overcomes the problems which exist in the prior art.

According to a first aspect of the present invention, this provides a method for determining the presence of oxygen in an environment comprising providing luminescent material whose intensity and lifetime of luminescence is quenchable by oxygen, incorporating said material in a carrier material which is relatively permeable to oxygen and relatively impermeable to interfering quenchers, thereby forming a sensor, exposing the sensor to an environment to be sampled, allowing oxygen in the environment to permeate the carrier material and quench the luminescent material, measuring the quenching-related decrease in intensity or lifetime of luminescence, and determining the presence of oxygen based on the measured quenching.

The oxygen concentrations can be in liquid solutions or in the gas phase. The method is based on the shortening of the lifetime or decrease in the emission intensity, i.e., quenching, or particular metal complexes, preferably ruthenium (II) complexes with α -diimine ligands in the presence of oxygen. The oxygen concentrations can be directly related to the degree of quenching. To prevent the complexes from responding to contaminants and interferents, the complex is protected by being immobilized in a gas permeable, solvent impermeable polymer, such as silicon rubber.

The oxygen determination method of the invention is non-destructive and relatively non-intrusive and which readily lends itself to miniaturization and automation. Furthermore the method of oxygen determination is based on a quencher-related decrease in lifetime of the luminescence of a luminescent material and requires no reference. It may be modified to provide a method of oxygen determination which is based on a quantitative quencher related decrease in the luminescence intensity of a luminescent material.

According to a second aspect of the present invention sensor apparatus for determining the presence of oxygen in an environment comprises luminescent material whose intensity and lifetime of luminescence is quenchable by oxygen, said luminescent material being incorporated in a carrier material which is relatively permeable to oxygen and relatively impermeable to interfering quenchers. This provides an oxygen concentration

sensor and a graded calibration standard which can be visually compared to determine oxygen concentration. The sensor is a fluorophor immobilized in oxygen-permeable polymer. The

- 5 graded calibration standard is either tapered with thicker (brighter) portions corresponding to lower oxygen concentrations on the sensor or with higher (brighter) concentrations of a fluorophor at one end of the standard. The sensor and standard are exposed to the environment being sampled and are excited by a light source. Intensity of the light emitted by the sensor is decreased by the oxygen. The eye, or an electronic detector is used to determine the part of the standard that has the
- 10 same brightness as the sensor.

- 15 The oxygen sensor may have a platinum group metal complex with α -diimine ligands immobilized in an oxygen permeable polymer which tends to prevent interfering quenchers from interacting with the complexes. Both the method and apparatus of the invention provide an inexpensive way of visually determining the extent of quenching.

- 20 The method and apparatus of the invention will now be described, by way of example only, with reference to the accompanying drawings. In the drawings:

- 25 Figure 1 is a schematic diagram, in side view, of a visual oxygen monitoring system embodying features of the present invention,

- 30 Figure 2 is a top plan view of sensor and reference devices shown in Figure 1,

- 35 Figure 3 is a detailed schematic diagram of a reference device used with the system shown in Figures 1 and 2, and

- 40 Figure 4 is a detailed schematic diagram of an alternative reference device used with the system shown in Figures 1 and 2.

- 45 The method of the invention is based on the principle of shortening of the lifetime or decrease in the emission intensity (quenching) of certain luminescent materials in the presence of oxygen. The oxygen concentrations can be directly related to the degree of quenching in a manner well known in the art.

- 50 The luminescent materials are luminescent inorganic materials which luminesce when excited with visible or ultraviolet light and whose luminescence is quenchable by oxygen and other quenchers.

- 55 The preferred luminescent materials are principally platinum group metal complexes, specifically, ruthenium, osmium, iridium, rhodium, palladium, platinum, rhodium and chromium complexes with α -diimine ligands. In most instances, the tris complexes are used, but it is recognized that mixed ligand complexes can also be used to provide a degree of design flexibility not otherwise available. Suitable ligand metal
- 60 complexes include complexes of ruthenium(II), osmium(II), iridium(III), rhodium(III), and chromium(III) ions with 2,2'-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-(1,10-phenanthroline), 4,7-dimethyl-1,10-phenanthroline
- 65 4,7-disulfonated-diphenyl-1,10-phenanthroline, 5-

bromo-1,10-phenanthroline, 5-chloro-1,10 phenanthroline, 2,2'-bi-2-thiazoline, 2,2'-bithiazole, and other α -diimine ligands.

- 70 Other suitable systems could include porphyrin or phthalocyanine complexes of VO^{2+} , Cu^{2+} , Pt^{2+} , Zn^{2+} and Pd^{2+} or dimeric Rh, Pt, or Ir complexes. Suitable ligands would be etioporphyrin, octaethylporphyrin, porphyrin and phthalocyanine.

- 75 To prevent the complexes from responding to contaminants and interferants, the complex is protected by being immobilized in a gas permeable, solvent impermeable polymer. Preferred polymers include that known under the trade name plexiglass, polyvinyl chloride (PVC), polystyrene, polycarbonate, latex, fluorinated polymers such as that known under the registered Trade Mark Teflon, and silicon rubbers, such as GE RTV SILASTIC 118 (RTM), which is very temperature resistant. A sensor using
- 80 SILASTIC 118 (RTM) exhibits a substantial change in lifetime or intensity of luminescence on going from an oxygen saturated environment to a deoxygenated environment. The precision and accuracy of oxygen determinations is about 2 per cent and the same responses are obtained for
- 85 both lifetime and intensity quenching measurements. It responds rapidly to changes in both gas phase and solution dissolved oxygen concentrations. The plexiglass and PVC systems have lower oxygen sensitivities and are, thus,
- 90 suitable for determinations at high (above atmospheric) oxygen pressures. Commercially available silicon rubber has a high permeability of oxygen and excludes highly polar compounds and hydrated ions which is why its use in the present invention is desirable.

- 95 The preferred oxygen sensor used tris(4,7-diphenyl-1,10-phenanthroline ruthenium(II) dissolved in the SOLASTIC 188 (RTM) material.

- 100 The luminescent complexes can be uniformly diffused into the polymer from dichloromethane and/or alcohol solutions. Alternatively, the complexes can be mixed with the polymer before final polymerization.

- 105 The metal complexes can be mechanically or chemically incorporated into the polymer matrix. In one embodiment, the complex molecules are chemically attached to the backbone of the matrix. Either a covalent or an ionic attachment of the complex to the polymer can be used. For example, cation exchange bound Ru(II) complexes exhibit high sensitivity to gas phase oxygen quenching.

- 110 The completed sensor is an integral device having the luminescent material incorporated directly into the self-supporting polymer barrier system. It can be in the form of a strip, a block a sheet, a microsphere, a film or a laminate and it can be either solid or hollow. If desired, the sensor
- 115 can be a thin sensing layer diffused onto a thick plate. An overcoat of a less reactive polymer can be used to further reduce interactions with the solvent or quenchers.

- 120 In one embodiment, a thin film sensor is formed by leaching sodium from glass to form a
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- 130

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porous matrix, dipping the glass into a solution of luminescent material and then covering the surface of the glass with a layer impermeable to water. Suitable agents are silicon water proofing which reacts with the surface or polymer overcoats.

To reduce expenses, it is desirable that the sensor be in the form of reusable polymer coated cuvettes which are highly durable.

In use, the sensor is exposed to the liquid or gaseous environment being sampled. Because the polymer material has a relatively high permeability to oxygen, the oxygen will permeate through the material and interact with the luminescent material to act as a quencher. However, the polymer will exclude most common ionic and organic interferents and contaminants.

The quenching-related decrease in the intensity or lifetime of luminescence is measured and that measurement is used to determine the concentration of oxygen in the environment. By measuring the luminescence lifetime or intensity using a back scattering technique, interferences caused by strong scattering or absorbing solution are eliminated.

In an alternative embodiment, the sensor is excited by a modulated light source and a phase shift measurement is made of the luminescence to yield the lifetimes.

The present invention provides a particularly desirable means for oxygen determination because it is non-invasive and does not consume oxygen. It is usable over an extremely wide range of oxygen concentrations or partial pressures and readily lends itself to miniaturized and automated analyses.

Test results have demonstrated that the present invention is sensitive, selective and readily implemented. With the preferred combination of metal complex and polymer matrix, a material has been prepared that shows a 3000% increase in luminescence lifetime on going from an oxygen saturated aqueous environment to a nitrogen saturated environment. Response time is subsecond to minutes depending on film thicknesses. The same complex-polymer sensor responds equally well to gas phase oxygen concentrations. Films of 0.001" thickness have been shown to respond in <1/6 sec. and follow faithfully the oxygen concentration in the breath of a human.

The ability of the polymer to protect the complex from interferents was shown by introducing a film into a concentrated solution of iron(III). Normally iron(III) is an excellent quencher of unprotected complexes. Yet, even at the high iron(III) concentrations used, there was no detectable quenching. Strong acid strong base, complexing agents (EDTA), and detergents (NaLS) were likewise without effect. The sensor is also immune to any deactivation by common anaesthetic gases such as Halothane and nitrous oxide at concentrations well above those used medically.

Applications for the present invention include: (1) measuring dissolved oxygen in aqueous samples and in organic solvents; (2) determining the oxygen for biochemical oxygen demand (BOD) measurements; (3) measuring levels of oxygen in blood both *in vitro* and *in vivo* using a fibre-optic probe; (4) measuring oxygen levels in air samples (e.g., mines, industrial hazard areas, oxygen tents, high pressure oxygen burn treatment and decompression chambers, industrial reactors space capsules etc); (5) measuring low oxygen levels in vacuum systems (i.e., a low-cost vacuum gauge); and (6) monitoring low oxygen levels in various chemical reaction vessels, e.g. glove boxes and other systems purged with inert gas. An application in Category 1 would include pollution monitoring of waste water.

The application in Category 2 is especially interesting in view of the above described test using iron(III). Iron(III) is added as a nutrient in BOD determinations. However, the test showed that iron(III) concentrations hundreds of times larger than would be encountered in BOD analyses have no detectable quenching effect. BOD determinations using quantitative intensity monitoring have been implemented.

The Category 3 applications could involve, for example, the placing of a sensor at the end of a fibre optic catheter for use in following oxygen concentrations in blood vessels and tissues as the heart is beating. Such a system has great safety as there is no electrical connection to the patient.

Advantages of the present invention are that it is a non-destructive and relatively non-instrusive method and that a common system can be used to measure oxygen in polluted, murky water, air samples, vacuum systems and other diverse types of systems. The invention is operable over a temperature range of about -300°F to about 400°F.

In addition, the system lends itself readily to measurements on very small sample size (<50 μ L) instrumental miniaturization, and automation. By encapsulating the complex probe in microscopic beads, oxygen concentrations can be measured under a microscope in growing cellular samples.

Quantitive intensity and lifetime methods for measuring oxygen concentrations are accurate and precise. There are many times, however, when a semiquantitative or qualitative method of even lower cost is desirable.

To avoid the cost of a more elaborate instrument the present invention further provides a low cost visual detection system with an internal reference for semiquantitative or qualitative oxygen monitoring.

In the present invention, the human eye is used as the detector. The scheme is similar in application to pH paper except that one monitors oxygen concentrations by comparing the emission intensity of the sensor in the gas or liquid environment to a series of reference emitters in that environment. Although suitable for semi-quantitation of oxygen concentrations, the system is also usable as a go-no go system where

instantaneous visual discrimination between pure oxygen, air, or an oxygen-free system is required.

A schematic diagram of this system is shown in Figures 1 to 4 to which reference is now made.

5 A luminescent oxygen sensor 10 and a reference emitter 12 are paced side-by-side in the sample fluid or gas environment 14. The sensor 10 includes a fluorophor immobilized in an oxygen-permeable support, in this example, a polymer. The sensor 10 luminesces when the fluorophor is excited by a light source 16. The intensity of the emitted light is decreased by oxygen in the environment 14 which serves as a quencher.

15 The human eye can easily judge the differences in intensity of the emitted light when the sensor film is exposed to pure N_2 , air and O_2 environments.

20 The estimation of the oxygen concentration beyond air, O_2 or N_2 is improved by using a reference emitter 12 which is a concentration or optical density graded calibration standard. In the standard, the same fluorophor as used in the sensor 10 would be immobilized in a rigid polymer, for example that known under the Trade Name plexiglass, which shows limited permeability to O_2 . The fluorophor is distributed in the polymer in areas having different luminescence levels.

30 The reference emitter 12 next to the sensor 10 provides reference concentration information by emitting reference luminescence levels. The differences in luminescence between the sensor 10 and the reference 12 are visually determined by the human eye 18. An optional blocking filter 20 can be positioned between the eye 18 and the sensor 10 and reference 12 to improve viewing contrast by removing scattered excitation light. In addition, a filter (not shown) over the light source 40 may be used to improve viewing by limiting excitation wavelengths.

45 In one embodiment, the standard 12' has a tapered wedge shape as shown in Figure 3. The luminescence intensity at each point is determined by the thickness of the standard 12'. The thicker (brighter) portions correspond to lower oxygen concentrations on the sensor 10. A non-uniform slope on the wedge improves the linearity of calibration.

50 In an alternative embodiment, the standard 12" is a concentration graded reference with the concentration of fluorophor contained therein increasing from one end to the other. The higher (brighter) concentrations correspond to lower oxygen concentrations on the sensor. In the graded standard 12" shown in Figure 4, the relative concentration of the fluorophor is indicated by the dot density. The sensor 12" is of uniform thickness.

60 The graded concentration standard 12" can be formed by withdrawing a polymer film from a solution containing the fluorophor material. The areas of the film which remain longer in the solution contain greater concentrations of the fluorophor.

In the preferred embodiment, the sensor 10 and the reference 12 are formed of identical luminescent materials. This ensures that the emission colours are the same and that the observer will only be comparing intensities.

70 Fluorophors suitable for use in the present invention include, but are not limited to, the metal complexes discussed above. The preferred material is tris(4,7-diphenyl)-1,10-phenanthroline)ruthenium(II) immobilized in a silicon rubber polymer matrix. Other fluorophors and polymer matrices will give greater or lesser sensitivity.

80 The system shown in the figures is used by allowing the oxygen in the environment 14 to impinge upon the sensor 10 and reference 12. The support matrix in the sensor 10 is permeable to oxygen, and thus allows the oxygen to quench the luminescent material. The matrix in the reference 12 restricts oxygen access to the fluorophor material therein. The luminescence of the quenched sensor 10 is then compared to the luminescence of the reference 12. The area of the reference 12 having the same luminescence as the sensor 10 is then visually selected. Knowledge of the amount of luminescent material present in the selected area is used to determine the amount of oxygen present in the environment 14. With proper calibration, a visual match of emission intensity can allow oxygen estimations to within a few per cent.

95 For sensor 10, films of 0.001" thickness, the response time is subsecond. Thicker sensor films respond more slowly and provide indications of average oxygen concentrations.

100 In an alternative embodiment, the present invention contemplates the use of a self-referencing sensor. Such a sensor includes a mixture of fluorophors which have differing sensitivities to oxygen quenching and differing colours of emission. By suitably adjusting the characteristics, the sensor is made to change colours at different oxygen concentrations. It is thus possible to completely dispense with the reference emitter 12 used with the system described above. The self-referencing sensor is especially useful in go-no go applications.

110 The referencing systems described above are inexpensive and provide stable, long-lasting, rapid monitors for gaseous or liquid oxygen levels. They can be incorporated into operating room gas lines, breathing masks, and other hospital devices where the shut-off or improper connection of oxygen could be fatal. They can also be used in mines and industrial areas where oxygen levels vary. Applications as far-reaching as space capsules and as ordinary as welding machines (He-arc purges) are also contemplated.

Claims

125 1. A method for determining the presence of oxygen in an environment comprising providing luminescent material whose intensity and lifetime of luminescence is quenchable by oxygen, incorporating said material in a carrier material

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which is relatively permeable to oxygen and relatively impermeable to interfering quenchers, thereby forming a sensor, exposing the sensor to an environment to be sampled, allowing oxygen in the environment to permeate the carrier material and quench the luminescent material, measuring the quenching-related decrease in intensity or lifetime of luminescence, and determining the presence of oxygen based on the measured quenching.

2. A method as claimed in Claim 1 wherein the environment is a gas.

3. A method as claimed in Claim 1 wherein the environment is a liquid.

4. A method as claimed in any preceding claim wherein the concentration of oxygen in the environment is determined.

5. Sensor apparatus for determining the presence of oxygen in an environment comprising luminescent material whose intensity and lifetime of luminescence is quenchable by oxygen, said luminescent material being incorporated in a carrier material which is relatively permeable to oxygen and relatively impermeable to interfering quenchers.

6. Apparatus according to Claim 5 wherein the luminescent material is an inorganic material.

7. Apparatus according to Claim 5 wherein the luminescent material is a phosphorescent material.

8. Apparatus according to Claim 5 wherein the luminescent material is a platinum group metal complex.

9. Apparatus according to Claim 5 wherein the luminescent material is selected from the group consisting of vanadium, copper, ruthenium, rhodium, osmium, iridium, rhodium, platinum, palladium, zinc and chromium complexes with α -diimine ligands, porphyrins, phthalocyanine and other ligands.

10. Apparatus according to Claim 9 wherein the complexes are selected from the group consisting of mixed ligand complexes, dicyano complexes and tris complexes.

11. Apparatus according to Claim 9 wherein the luminescent material is selected from the group consisting of complexes of ruthenium(II), osmium(II), iridium(III), rhodium, rhodium, and chromium(III) with 2,2'-bipyridine, 1, 10-phenanthroline, 4,7-diphenyl(1,10-phenanthroline), 4,7-dimethyl-1, 10-phenanthroline, 4,7-disulfonated-diphenyl-1, 10-phenanthroline, 2,2'-bi-2-thiazoline, 2,2'-bithiazole, 5-bromo-1,10-phenanthroline, and 5-chloro-1,10-phenanthroline and 5-chloro-1,10-phenanthroline and complexes of VO(II), CU(II), platinum(II), and zinc(II) with porphyrin, etioporphyrin tetraphenylporphyrin, mesoporphyrin IX dimethylester, proto porphyrin IX dimethylester and octaethylporphyrin.

12. Apparatus according to Claim 9 wherein the luminescent material comprises tris(4,7-diphenyl-1,10-phenanthroline)-ruthenium(II), tris-(disulfonated-(4,7-diphenyl-1),10-

phenanthroline)ruthenium(II), and (disulfonated-4,7-diphenyl-1,10-phenanthroline)bis(1,10-phenanthroline)-ruthenium(II).

13. Apparatus according to any one of Claims 5 to 12 wherein the carrier material comprises a polymer in the form of sheets, films, blocks, laminates, microspheres, tubes and strips.

14. Apparatus according to Claim 13 wherein the polymer is selected from the group consisting of plexiglass, polyvinyl chloride, silicon rubber, natural rubber, polycarbonate, teflon, polystyrene, polyvinylidene fluoride, poly(tetrafluoroethylene propylene) and cation and anion exchange resins.

15. Apparatus according to Claim 13 or 14 wherein the luminescent material is incorporated into the polymer by a process selected from the group consisting of diffusing the luminescent material into the polymer from suitable organic solution, mixing the luminescent material with the polymer before final polymerization, and ionically or covalently binding the luminescent material to the polymer.

16. Apparatus according to any of claims 13 to 15 wherein the polymer is protected further from the solvent by overcoating it with an oxygen permeable solvent resistant polymer such as Teflon.

17. Apparatus according to any one of Claims 5 to 12 wherein the carrier material comprises a porous adsorbant polymer such as silica gel, alumina etched glass, or controlled porosity glass.

18. Apparatus according to Claim 17 wherein the luminescent material is incorporated into the adsorbant by diffusion from a penetrating solvent and held by adsorption, ionic binding, or covalent chemical attachment to the adsorbant.

19. Apparatus of Claim 17 wherein the polymer is protected from the solvent by an overcoat of solvent impermeable material which can include silicon oils or chemical silinization of the surface.

20. Apparatus for determining the amount of oxygen in an environment comprising sensor apparatus as claimed in any one of Claims 5 to 19, a reference device having said luminescent material distributed therein in areas having differing amounts of said material, said sensor and said reference device being arranged in a proximate relationship, said sensor and said reference device being arranged to be exposed to an environment to be sampled, oxygen in the environment being arranged to quench the luminescent material in the sensor, oxygen access to the luminescent material in the reference device being restricted, comparing the luminescence of the sensor with the luminescence similarity of luminescence between the sensor and an area of the reference device being compared to determine the amount of oxygen in the environment based on the amount of luminescent material present in said area of the reference.

21. Apparatus according to Claim 20 wherein the reference comprises a support having luminescent material distributed therealong in

areas having differing amounts of said material, said luminescent material being the same as the sensor material that is quenchable by oxygen.

22. Apparatus according to Claim 21 wherein said luminescent reference material is distributed in areas of differing thickness.

23. Apparatus according to Claim 21 or 22 wherein the reference has a wedge or staircase shape, the amount of luminescent material present in any portion of said wedge or staircase being related to the thickness of said portion.

24. Apparatus according to Claim 23 wherein the wedge or staircase has a non-uniform slope or step size.

25. Apparatus according to any of Claims 21 to 24 wherein the luminescent material is distributed to form areas having differing concentrations of said luminescent material.

26. Apparatus according to any of Claims 20 to 25 wherein the luminescent material comprises fluorophor material.

27. Apparatus according to any one of Claims 20 to 26 wherein the reference device is formed of material which is relatively impermeable to oxygen, said luminescent material being incorporated into the support material.

28. Apparatus according to any one of Claims 20 to 27 wherein the reference is formed by withdrawing the support from a solution of luminescent material, the concentration of luminescent material in a given area of the support being related to the length of time the area remains in said solution or alternatively, the sensor concentration would be related to the changing concentration in the solvent as the support is withdrawn.

29. Apparatus as claimed in any one of Claims 5 to 28 in which the carrier material includes a support containing a mixture of luminescent materials quenchable by oxygen, said materials of the mixture having differing sensitivities to oxygen

quenching and having differing colours of emission.

30. Apparatus according to any one of Claims 5 to 29 using the phase shift of the luminescence of material relative to a modulated excitation source to measure the lifetime and relate it to the oxygen concentration.

31. Apparatus as claimed in any one of Claims 5 to 30 wherein the sensor responds to gases other than oxygen, for example sulphur dioxide, carbon dioxide and chlorine.

32. A method of determining the amount of oxygen in an environment comprising sensor apparatus as claimed in any one of Claims 5 to 19, a reference device having said luminescent material distributed therein in areas having differing amounts of said material, said sensor and said reference device being arranged in a proximate relationship, said sensor and said reference device being arranged to be exposed to an environment to be sampled, oxygen in an environment being arranged to quench the luminescent material in the sensor, oxygen access to the luminescent material in the reference device being restricted, comparing the luminescence of the sensor with the luminescence similarity of luminescence between the sensor and an area of the reference device being compared to determine the amount of oxygen in the environment based on the amount of luminescent material present in said area of the reference.

33. A method of determining the presence of oxygen in an environment substantially as hereinbefore described and with reference to the accompanying drawings.

34. Apparatus for determining the presence of oxygen in an environment substantially as hereinbefore described, and with reference to Figures 1, 2 and 3 or Figures 1, 2 and 4 of the accompanying drawings.

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